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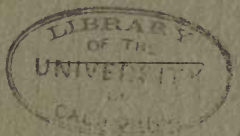
An Investigation of Zinc Amalgams and Concentration Cells

A THESIS

SUBMITTED TO THE FACULTY OF PRINCETON UNIVERSITY IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY.



BY

J. L. CRENSHAW

EASTON, PA.:
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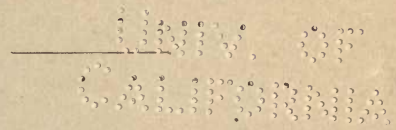

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An Investigation of Zinc Amalgams and Concentration Cells

Introduction

Although the first investigation of zinc amalgams was undertaken more than fifty years ago[1] and a vast amount of work has been done since that time in this very important field,[2] nevertheless at the time the present research was undertaken very few accurate and no complete data on the subject were obtainable.

In 1877 Helmholtz[3] in his epoch-making paper developed the theory of concentration cells from a thermodynamic point of view and twelve years later Nernst,[4] from a purely physical-chemical standpoint, worked out his equation for the electromotive force of concentration cells. G. Meyer[5] and von Turin[6] were the first to confirm the theoretical formula by the results of experiment by working with amalgam concentration cells. The special interest taken in a study of these cells is largely due to the fact that they are the simplest kind of primary cells and therefore offer the most promising field for rigidly verifying our theories or of explaining any observed discrepancy between the theoretical and experimental values obtained.

Previous workers have restricted themselves to a relatively small range of concentration on account of the experimental difficulties involved in preparing and handling amal-

[1] Guigain: Compt. Rend., 42, 430; Becquerel: Ann. Chim. Phys., 48, 266 (1856).

[2] Hockin and Taylor: Jour. Soc. Tel., 282 (1872); Lindeck: Wied. Ann., 35, 311 (1888); von Turin: Zeit. Phys. Chem., 5, 340 (1890); Richards and Lewis: Zeit. Phys. Chem., 28, 7; Cady: Jour. Phys. Chem., 2, 551 (1898); Trevor: Jour. Phys. Chem., 3, 95 (1899).

[3] Monatsberichte d. Kgl. Preuss. Akad., Berlin, 1877.

[4] Zeit. Phys. Chem., 4, 128 (1889).

[5] Wied. Ann., 40, 244 (1890).

[6] Zeit. Phys. Chem., 5, 340 (1890).

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gams, but the work done in this laboratory has made it possible to avoid these difficulties so that the present investigation extends over the greatest range possible, the limits of the concentration being an amalgam saturated with zinc on the one hand and an amalgam of zero concentration or pure mercury on the other. The more dilute amalgams in this range had never been investigated and it was thought very likely that dilutions of the order of one part of zinc to ten million or one hundred million parts of mercury would give some very interesting information on the equilibrium between mercury and a zinc sulphate solution, such as was obtained by Hulett and De Lury on cadmium amalgams.[1] It is well known that a rod of zinc becomes coated with mercury when placed in a solution containing a mercury salt. If this reaction is reversible, as of course it must be if our ideas of chemical equilibrium are correct, we should expect that mercury, when put into a zinc sulphate solution, would precipitate some zinc and become a very dilute amalgam. This expectation was substantiated by the experimental results as will be shown in the following pages.

One of the most serious difficulties encountered by previous investigators has been due to a loss of zinc from the amalgams by oxidation and unless this difficulty is overcome the results are not reliable. The more recent workers paid a great deal of attention to this point, but they were not in a position to know just how successful their precautions were since they were measuring the electromotive force of these amalgams in a concentration cell and this magnitude depends on the relative and not on the absolute concentrations of the amalgams so that there might have been a loss of zinc from all of the amalgams in the cells and, provided this loss in each case was proportional to the concentration, there would have been no change in the electromotive forces of the cells.

In the present work we employed a two-phase reference electrode in each cell. This electrode was of such a nature

[1] Jour. Amer. Chem. Soc., 30, 1805 (1908).

that its potential was independent of a loss or gain of zinc but depended only on the temperature, therefore it was exceedingly reproducible and constant. With this electrode as a basis we were able to detect at any time a loss of zinc from any of the unsaturated amalgams and thus we were enabled to rigidly control each step of the experiment.

The difficulty in making and handling the amalgams as well as the problem of excluding the oxygen has been overcome in this and previous work[1] done in this laboratory. Since all these things are of primary importance in obtaining reliable results, the apparatus and methods will be described in considerable detail in this thesis.

Purification of Materials.—All of the mercury used in this investigation was chemically purified and then distilled by the method devised by Hulett.[2] In this method a continuous stream of air is allowed to bubble through the mercury which is distilled under diminished pressure. The air is essential to this process as otherwise both zinc and cadmium distil over if present.

Mylius and Fromm[3] have succeeded in obtaining very pure zinc and their most satisfactory method, with slight modifications, was the one used in this work. The zinc sulphate was first dissolved and then treated with Kahlbaum's best zinc oxide, hydrogen peroxide and electrolytic ozone being used to oxidize any *ous* iron. After digesting two or three days on a water bath all of the iron was considered precipitated. The solution was then filtered, made slightly alkaline with ammonium hydroxide and treated with hydrogen sulphide until a fairly heavy precipitate of zinc sulphide was obtained. This was then digested for two or three days on a water bath with frequent agitation which insured the complete precipitation of the heavy metals. The solution was then filtered and the zinc sulphate crystallized out. This

[1] Hulett and De Lury: Jour. Amer. Chem. Soc., 30, 1805 (1908).
[2] Phys. Rev., 21, 388 (1905).
[3] Zeit. anorg. Chem., 9, 176 (1895).

purified zinc sulphate after crystallizing and centrifuging three times was used as the electrolyte from which our electrolytic zinc was obtained. The anode used was a piece of platinum foil of about 6 cm^2 area. This was enclosed in a filter paper anode cup. In order to keep the solution from becoming acid during the electrolysis the anode cup was kept full of a basic sulphate of zinc prepared in the following manner: ammonium hydroxide was added to a solution of the purified zinc sulphate until the precipitate at first formed redissolved. This clear solution was then allowed to drop slowly into boiling water, a steady stream of steam being passed in to prevent bumping. A white crystalline precipitate was obtained that could be readily filtered and washed. The cathode was a tenth mm. platinum wire sealed into a small glass tube so that about only one-half mm. protruded. The current was regulated by resistance, the density being kept low enough to obtain a compact deposit of zinc. The zinc thus obtained, after being washed and dried, was melted in a hard glass tube with ammonium chloride (specially purified) which took care of the dross and inclusions and left the zinc clean and bright at the bottom. This ingot was carefully scraped with clean steel and then melted in a high vacuum to remove any volatile impurities. It was then transferred to another hard glass tube and distilled in vacuum. The distillation was always stopped before all of the zinc had distilled over. The distilled portion was run into the drawn out end of the tube and kept sealed up until used. In the distillation of zinc it was found necessary to continue the evacuation until the zinc started to distil over, otherwise all the gases were not removed and the tube softened before the distillation temperature was reached.

In the purification all cork and rubber stoppers and connections were carefully avoided and when connections were necessary the glass was sealed together. The solutions were always kept in Jena flasks.

Preparing and Handling the Amalgams.—The masses of mercury and zinc necessary for making an amalgam of any

given concentration can be very accurately weighed out on the balance, but the difficulty of mixing the two metals without a loss of zinc by oxidation has been a very serious obstacle. This has been overcome by the following very simple device first used by Hulett and De Lury.[1]

A short piece of glass rod (a) Fig. 1 was sealed onto the

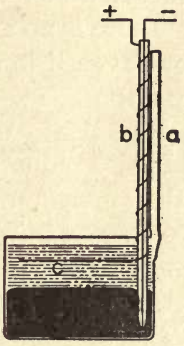

Fig. 1

edge of a small crystallizing dish. The glass tube (b) had a platinum wire sealed into its lower end and extending up through the tube. Another platinum wire (c) extended across the center of the dish and was sealed onto the outside of the tube (b). The tube was fastened securely to the upright rod, (a), by means of insulating tape or a little marine glue and thus formed a very compact piece of apparatus. The mass of zinc to be used in a given amalgam was weighed out on a balance sensitive to 0.01 mg. The mass of mercury required for a given concentration was then calculated and weighed out. All weighings were made by substituting calibrated weights for the tared metal. The vacuum correction was applied to the weights of mercury but since the density of zinc was about the same as that of the weights the vacuum correction for it was negligible. After weighing, the mercury was put in the apparatus just described (Fig. 1) and made cathode by twelve volts under distilled water. The weighed pieces of zinc were

[1] Loc. cit.

now dropped on the mercury, and dissolved without forming a coat. All the amalgams made up in this way presented a surface as clean and bright as pure mercury and could be preserved for any length of time. Amalgams were thus made up of very exact composition without the slightest chance of a loss of zinc by oxidation. It has been suggested that the mercury distilled by the process which we employed might contain dissolved oxygen.[1] There is no evidence of the solubility of oxygen in mercury, but even if it were found to be soluble there is no question that the e. m. f. applied in the above method of preparing the amalgam would rapidly depolarize any dissolved oxygen. It also reduces any coat of oxide that might have formed on the amalgam.

Density and Composition of Zinc Amalgams.—It was desirable to know the concentration of zinc in the liquid portion of the standard electrode at the temperature of the e. m. f. measurements, 25°. The work of Richards and Forbes[2] on the density and composition of zinc amalgams at 20° indicated that the density was a linear function of the composition, but their results extended only over a limited range. We have found that the density, at 25° is a linear function of the composition from pure mercury up to the saturated amalgam. This curve was accurately located so that it was only necessary to know the density of an amalgam to calculate its composition.

The pycnometer used (Fig. 2) was of the same form as

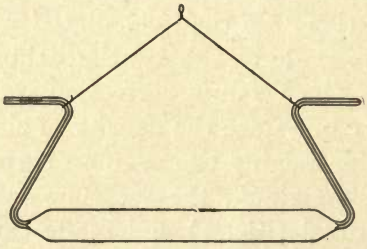

Fig. 2

[1] T. W. Richards, Carnegie Pub., 118, p. 8.
[2] Zeit. phys. Chem., 58, 693 (1907).

that used by Hulett and De Lury[1] which was found to have many points of advantage over the ordinary type. One of the capillary tubes had a single mark near the end while the other was marked off into twenty-one equal divisions. This graduated end was carefully calibrated so that it was only necessary to adjust the amalgam to the single mark on the other end. Each division on this stem was 0.708 mm. The capillary was filled with varying amounts of mercury and the length of the column and the weight were carefully determined. Three determinations gave as the weight of one division: 0.00230, 0.00228 and 0.00231 respectively. If we take 0.00230 as the weight of mercury required to fill one division and the density of mercury at 25° as 13.53396 the volume of one division of the stem is found to be 0.00017 cc.

This pycnometer was weighed frequently during the time it was used. For example it was weighed five times on as many successive days, three of these weighings were exactly the same 15.9621 the other two were 15.9623 so that 15.9622 was considered very near the true weight. The average of five weighings of this pycnometer filled with mercury to the 21st division at 25° gave 107.24385. This gives 91.26261 as the mass of mercury in the pycnometer and from this the volume at 25 is calculated to be 6.7432 cc. The pycnometer was then filled to the 7th division of the capillary and found to weigh 107.21124 which gave as the mass of mercury 91.23000 giving 6.7408 as the volume to the 7th division. The difference of these two volumes 0.0024 cc. should be equal to the volume of the fourteen unfilled divisions of the capillary. The volume of one division was found to be 0.00017 so that the volume of fourteen divisions would be 0.00238 showing the two results to be in perfect agreement.

The densities of amalgams of four different concentrations were determined with this pycnometer. The amalgams containing respectively 1, $1^1/_2$ and 2 grams of zinc in 100 grams of mercury were made by weighing out very accurately

[1] Loc. cit.

the required amounts of zinc and mercury for the different concentrations. The zinc was weighed out first on a balance sensitive to 0.01 mg., the air weight of mercury required was then calculated and weighed out. By means of a fine capillary joined to a piece of rubber tubing the amount of mercury was easily adjusted to one or two tenths of a milligram.

Weight of zinc	1.48624	1.70912	3.12705
Weight of mercury	148.63247	113.94540	156.85811
Vacuum correction	0.00817	0.00626	0.00862
Mass of mercury	148.62430	113.93914	156.84949
Grams of zinc per 100 grams of mercury	0.999998	1.500028	1.993600

The saturated amalgam was made by rotating an excess of zinc with mercury in a 25° thermostat. The separation of the saturated amalgam from the excess of zinc without changing the temperature was effectively accomplished by the use of the piece of apparatus shown in Fig. 3. The mercury with

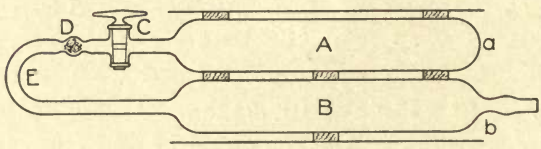

Fig. 3

an excess of zinc was placed in (A) through the end (a) which was then sealed off. The cock (C) was closed and an aspirator applied to (b). After the pressure in B had been reduced to about 3 cm. the thickened part at (b) was sealed off. This whole apparatus was then slipped into a large glass tube and rotated at 25° ±0.02 for several weeks, then without removing it from the bath the apparatus was held in a vertical position, the end (E) being down, and after standing one hour the cock (C) was slowly turned, the amalgam then passed into (B) through the filter (D), composed of asbestos well packed in. Since zinc floats on the amalgam and the amalgam is drawn off from the bottom there can be little doubt that this method effectively separated the two phases. As soon as sufficient of the amalgam had passed into (B) the apparatus was removed

from the bath, the tube (B) cut open and the amalgam brought into the apparatus (Fig. 1) and made cathode by 12 volts under distilled water until used.

To insure complete saturation the zinc and mercury were usually heated up to 50° or 100° with frequent agitation before the rotation began so that the equilibrium was approached from the higher temperature.

DENSITIES.

Composition	1/100	1.5/100	1.9936/100
Pycnometer + amalgam	106.66306	106.34468	106.04772
Pycnometer	15.97622	15.97622	15.97622
Weight of amalgam	90.68764	90.36846	90.07150
Vacuum correction	0.00498	0.00497	0.00495
Mass of amalgam	90.67286	90.36349	90.06655
	(to 18th)	(to 7th)	(to 3rd)
Volume of pycnometer	6.7427	6.7408	6.7401
Density	13.4490	13.4054	13.3628

DENSITY OF THE SATURATED AMALGAM.

From three tubes	A	B	C
Pycnometer + amalgam	105.95668	105.94731	105.95207
Pycnometer	15.97622	15.97622	15.97622
Weight of amalgam	89.98046	89.97109	89.97585
Vacuum correction	0.00495	0.00495	0.00495
Mass of amalgam	89.97551	89.96614	89.97090
Pycnometer division	(to 20th)	(to 17th)	(to 18th)
Volume of pycnometer	6.7430	6.7425	6.7427
Density	13.3435	13.3431	13.3434
Average	—	13.34333	—

Taking the density of pure mercury at 25°, (13.5340) and that of 1, $1^1/_2$, and 2 percent amalgams the density composition curve was plotted. The following relation is the result of the above determinations and represents very accurately the density of any amalgam. $D_{25°} = 13.5340 - 0.0859\ p$ where p is the number of grams of zinc in 100 grams of mercury. The point on this line which corresponds to the density of the saturated amalgam, 13.34333, indicates a composition of 2.2196 grams of zinc in 100 grams of mercury.

The composition of the saturated amalgam prepared as described above was also determined by analysis. The amal-

gam was treated with hydrochloric acid[1] (1 vol. conc. acid to 1 vol. of water) which dissolved the zinc with an energetic evolution of hydrogen and never dissolved a weighable amount of mercury unless the acid was allowed to stand in contact with the mercury many times longer than was necessary for the removal of the zinc. It was found necessary to hasten the reaction by means of a platinum spiral which made contact with the amalgam and extended up through the acid. A small glass bead was fused on the wire just above the point reached by the amalgam surface to prevent the mercury from creeping up the wire and destroying its effectiveness. After all of the zinc had been dissolved the acid was removed with a pipette and the mercury washed and dried in a vacuum desiccator over calcium chloride. It was found necessary to use every precaution to prevent a loss of mercury by "spurting" when the desiccator was evacuated. In order to dry the mercury effectively a comparatively high vacuum was necessary and if any particles of water happened to be under the mercury their rapid expansion threw a fine spray of mercury up against the sides of the flask and out of the top if uncovered. As much as twenty milligrams of mercury were often lost in this way. This difficulty was effectively overcome by providing the analysis flasks with loosely fitting stoppers, setting them in shallow dishes and covering them with inverted beakers when they were put in the desiccator. The following are the results of duplicate analysis of amalgams taken from two different tubes I and II.

	I.		II.	
Flask and amalgam	23.9132	28.1761	35.0044	51.0937
After treatment with acid	23.5386	27.8001	34.3882	50.2204
Mass of zinc	0.3746	0.3760	0.6162	0.8733
Flask	6.6599	10.8565	6.6600	10.8570
Weight of mercury	16.8787	16.9436	27.7282	39.3634
Mass of mercury	16.8778	16.9427	27.7267	39.3613
Grams of zinc in 100	2.2194	2.2192	2.2224	2.2186
Average	2.2193		2.2205	

[1] Kerp and Böttger: Zeit. anorg. Chem., **25**, 1 (1900).

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The average of these two values gives 2.2199 as the number of grams of zinc soluble in 100 grams of mercury at 25°. This value is in good agreement with the value 2.2196 calculated from the density-composition relations. These results are very probably reliable to the third place decimal so that 2.220 has been taken as the correct value.

The Coefficient of Expansion of Zinc Amalgams has also been measured. The dilatometer used consisted of a glass tube of about 8 cm. internal diameter and about 80 cm. long, to one end of which was sealed a capillary stopcock and to the other a capillary tube about 35 cm. long. A thermometer scale was fixed to this capillary tube and the instrument carefully calibrated with mercury. The weights of mercury required to fill it to various divisions of the scale at 25° were accurately determined and the volume thus calculated.

Division on scale at 25°	129.3	249.5
Air wt. of mercury	86.1477	86.3226
Mass of mercury	81.1430	86.3179
Volume	6.365 cc.	6.378cc.

The difference of these two volumes, 0.013 cc., should be equal to the volume of (249.5 – 129.3), 120.2 divisions of the capillary stem.

This capillary was calibrated separately:

501.5 divisions of mercury weighed 0.8002 g. wt. of 1 div. = 0.001425
328.0 divisions of mercury weighed 0.4673 g. wt. of 1 div. = 0.001425

From this, the volume of one division is found to be 0.000105 cc. and the volume of 120.2 divisions is 0.0126 cc., which is in fair agreement with the value of 0.013 obtained above. The dilatometer was now filled with mercury to the 224th division when at 25°; it was then put in a 35° thermostat and the mercury in the capillary rose to 317.2 on the scale. We may, within the error of the experiment, consider 0.000181 as the coefficient of cubical expansion of mercury. From this and the above data, the coefficient of cubical expansion of the glass is found to be 0.0000279, which is about the accepted value for the kind of glass used. A $1^1/_2$ percent amalgam was put in the dilatometer:

At 25.01° the amalgam reached to 260.5 on the scale.
At 35.03° the amalgam reached to 349.0 on the scale.

For a rise of 10.02° there was an increase of 88.5 divisions or 0.00929 cc. when the volume at the lower temperature was 6.379 cc. Taking into account the expansion of the glass as determined above, we get 0.000173 as the coefficient of cubical expansion of a $\frac{1^1/_2}{100}$ amalgam.

The density of a $\frac{1^1/_2}{100}$ zinc amalgam at 25° was found to be 13.4054. The density at 20°, calculated by means of the above coefficient, is, $D_{20} = \frac{13.4054}{1-(0.000173 \times 5)} = 13.4171$, giving a change of 0.0117 in density for a change of 5°. The change in density for pure mercury for the same range in temperature is 0.0122. The difference of 0.0005 in the two values is due to the presence of $1^1/_2$ grams of zinc in 100 grams of mercury. From this the difference which would be caused by 1 gram of zinc in 100 grams of mercury for a temperature change of 1° is calculated to be 0.000067.

The density of an amalgam at any temperature is given by the relation

$$D_t = D_{25} - (0.00244 - 0.000067\ p)\ (t - 25)$$

where D_{25} = density at 25°, p = grams of zinc in 100 grams of mercury, and t = temperature; or, combining this relation with the expression for the density of any amalgam at 25°, we have:

$$D_t = 13.5340 - 0.0859\ p - (0.00244 - 0.000067\ p)\ (t - 25).$$

Since the density is not a linear function of the temperature this equation applies only over a limited range of temperature.

Electromotive Force of Zinc Amalgams

No reliable observations could be obtained on the e. m. f. of dilute amalgams until means were devised for really removing and excluding oxygen. This is fundamental for all work with dilute amalgams. For this purpose it was very impor-

tant to have an adequate supply of hydrogen which was unquestionably free from oxygen.

The Preparation of Oxygen-Free Hydrogen.—The hydrogen was generated in a Kipp generator from Kahlbaum's No. II zinc and Baker's analyzed hydrochloric acid. The gas after passing through a tower containing soda lime and calcium chloride was conducted over a platinum spiral consisting of over a meter of tenth mm. platinum wire wound on a small porcelain tube. When hydrogen was being used this platinum wire was glowed continuously with an electric current and caused the hydrogen to combine with any residual oxygen. Nernst[1] and his co-workers have shown that in cases of this kind the gaseous mixture very rapidly comes to the equilibrium conditions corresponding to the temperature of the wire. They have also given us the necessary data for calculating the equilibrium constant for the equation $2H_2O \rightleftarrows 2H_2 + O_2$ for any given temperature. The temperature of the spiral was not far from 1000° absolute so that the calculated partial pressure of the oxygen in our hydrogen was of the order of magnitude of 4×10^{-16} mm. Oxygen then was practically out of the gas phase. All hydrogen passed over this glowing spiral immediately before it was used.

Cell.—The form of cell used is shown in Fig. 4. The

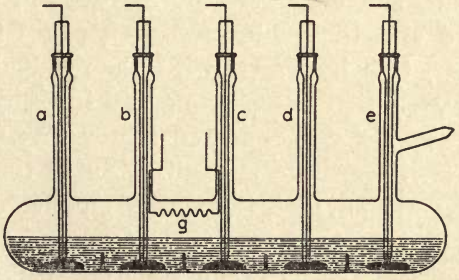

Fig. 4

cell was separated into compartments, by little dams about 1

[1] Thermodynamics and Chemistry; Nernst. Langmuir: Jour. Am. Chem. Soc., 28, 1357 (1906).

cm. high which prevented the mixing of the amalgams but allowed a thorough mixing of the electrolyte when the cell was rocked. The contact wires were short $^1/_{10}$ mm. platinum wires sealed into tubes which made well ground joints with the tubes a, b, c, d and e. The application of a very little marine glue made these joints perfectly tight. A little mercury was introduced into these tubes carrying the contact wires and made contact between the platinum wires and the copper wires which extended out of the cell. A spiral of $^1/_{20}$ mm. platinum wire (g) was fixed inside the cell by means of two larger lead wires sealed through the sides.

The side tube was connected by means of a T tube and two stopcocks to the hydrogen generator and a vacuum pump. The cell was first evacuated and then hydrogen was let in, this hydrogen with the residual oxygen was then removed by the vacuum pump and more hydrogen let in. This process was repeated until the air originally in the cell was replaced by hydrogen. The platinum wire (g) was then glowed to cause any residual oxygen to combine with hydrogen.

The Electrolyte.—The electrolyte was placed in a separatory funnel, the stem of which was connected, in the same manner as the cell was, with a vacuum pump and the hydrogen generator. The separatory funnel was first evacuated and the solution shaken vigorously in vacuum, hydrogen was then admitted and the solution shaken again to saturate it with hydrogen, this hydrogen with the residual oxygen was removed by evacuation and shaking and fresh hydrogen again let in. This process was repeated six or seven times before the electrolyte was put into the cell. One of the ground glass joints was then opened, after the marine glue had been warmed, and the oxygen free electrolyte was introduced against a rapid stream of hydrogen. The other materials which were introduced into the cells were also well washed by the hydrogen which was forced out through the tube through which they were introduced. The spiral (g) was continually glowing and took care of any oxygen which might have escaped these precautions.

The electrolyte in some cases was a saturated solution of zinc sulphate with an excess of zinc sulphate crystals covering the amalgams, in other cases a solution which was not quite saturated at 25° was used.

The amalgams up to a dilution of $\frac{1}{10^4}$ (that is one part of zinc to 10,000 parts of mercury) were made as follows. The zinc was cut into small pieces so that there was no especial difficulty in obtaining the correct mass of zinc for just enough of the given amalgam for one of the compartments of the cell. The mass of this zinc was determined to 0.01 mg. The air weight of mercury was then calculated and this amount of weights was placed on the balance pan together with a tube of the form shown in Fig. 5. The diameter of the largest part

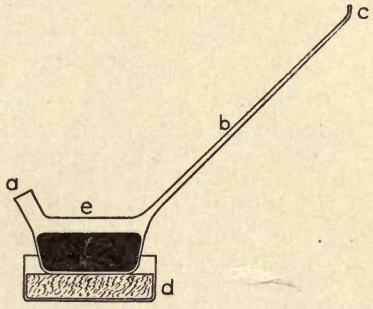

Fig. 5

of the tube was about 15 mm. The end (a) was drawn down to about 5 mm. and (b) to about 0.3 mm. internal diameter. The end (c) was closed and bent as shown. Just at the bend a scratch was made with a diamond. On the balance this tube rested on a cork support (d). After this tube and the weights were tared the weights were removed and the correct amount of mercury put into the tube, the last bit being adjusted with a capillary. The tube was now removed from the balance and (a) was connected by means of two stopcocks alternately with an aspirator and the hydrogen generator until the air about the mercury had been replaced with hydrogen.

One of the compartments of the cell was now opened and

the end (c) of the tube slowly introduced and thus washed externally with the stream of hydrogen which was forced in through the side tube and out through the opened tube (Fig. 4). By gently pressing the end of the tube (b) on the bottom of the cell, the end (c) was broken off at the point where it had been scratched and the mercury flowed down gently into the compartment under pressure of hydrogen from the generator.

The pieces of zinc were now held for some seconds in the stream of hydrogen issuing from the cell and then lowered slowly about half way down the tube to wash them with hydrogen; finally they were dropped into the mercury where they soon dissolved. This method could not be used for preparing amalgams more dilute than one part of zinc to ten thousand parts of mercury on account of the difficulty of weighing such a small amount of zinc with the required accuracy.

By comparing the potential of an amalgam made in this way with one of the same concentration made up outside of the cell and then introduced we have found that the method of making up the amalgam in the cell is the more reliable of the two, since it is almost impossible to introduce a very dilute amalgam without some oxidation taking place.

In the case of the more dilute amalgams the electrolyte and the two-phase amalgam were introduced in the manner just described; weighed amounts of mercury were put into the other compartments and after the ground joints were all sealed with marine glue the side tube was sealed off with a blowpipe. The wire (g) in the cell was brought to a glow with an electric current intermittently for three or four days, the contents of the cell being agitated continuously during this time. This was effected by an eccentric attached to a water motor which slowly raised and lowered one end of the cell causing the electrolyte to flow back and forth over the dams. The wire was glowed every few seconds instead of continuously because by this means less heat was generated in the cell.

As has been shown (p. 15) the glowing removed any residual oxygen in the gas phase and it seems that any trace

of dissolved oxygen in the electrolyte would have been completely removed by the agitation in an atmosphere of pure hydrogen and continually coming into contact with the two-phase amalgam. The cell was then put in the 25° bath and zinc from the two-phase amalgam was deposited electrolytically in the mercury. These two methods of making up the amalgams were made to overlap. That is two amalgams containing one part of zinc to ten thousand parts of mercury were made up, one by weighing out the metals directly and introducing them separately into the cell, the other by depositing the zinc electrolytically, and the potentials of the two were in excellent agreement.

Measurement of Electromotive Forces.—The basis of all e. m. f. measurements was Clark cells which had been made at intervals since 1903 and all of which were in good agreement. These cells are reproducible to better than one part in 50,000, their value was taken to be 1.42040 volts at 25°.[1] For this work a 100-liter oil bath was used. It was electrically heated and controlled and did not vary from 25° by more than 0.01° at any time. The thermometer used in locating this temperature was checked at the transition point of Glauber's salt, 32.383°.

The instruments used in the e. m. f. measurements were a high resistance Wolff potentiometer, a Broca glavanometer with 1000 ohm coils; a Nernst glower lamp and scale, a regulating resistance and two standard batteries[2] which gave a very steady and constant current. The resistance coils of the potentiometer were carefully calibrated and the whole system thoroughly insulated. Moisture or dust on the hard rubber base of the potentiometer introduced very considerable disturbances so the instrument was kept scrupulously clean and on damp days no measurements were taken.

The Standard Electrode.—Previous workers have observed that the e. m. f. between two dilute zinc amalgams of different concentrations increases considerably with the time. It is

[1] Phys. Rev., **32**, 275.

[2] Phys. Rev., **27**, 33 (1908).

obvious that this increase did not show the actual loss of zinc but only the relatively greater loss of the more dilute amalgam, since the e. m. f. depends only on the ratio of the two concentrations according to the equation, e. m. f. $= \frac{RT}{nF} ln \frac{C_1}{C_2}$, and if both amalgams lost zinc in proportion to their concentration there would be no change in e. m. f. This fact was pointed out by Hulett and De Lury[1] in their work on cadmium amalgams and they made use of a two-phase amalgam as a standard basis of reference for all potential measurements, since the potential of such an amalgam depends only on the temperature. This principle has been made use of in the present work and an amalgam containing about 5 percent of zinc has been used as the basis of all the potential measurements. It is well known that for a given temperature the potential of all zinc amalgams containing something over 2 percent of zinc is constant. Considerable loss of zinc by oxidation or from any cause could not, therefore affect the concentration or the potential of the standard electrode, so that any increase in e. m. f. between this standard and a dilute amalgam indicated a loss of zinc from the dilute amalgam *only* and the exact amount of this loss could be easily calculated.

The cells used for the amalgams had five or six compartments and each amalgam was measured against the constant electrode. The e. m. f. between any two amalgams was given then by the difference between e. m. f.'s as measured against the constant electrode. This method of measurement is the only one as yet employed by which one can be sure as to whether any amalgam is losing zinc. The values obtained by taking the difference between the e. m. f.'s of two amalgams against the constant electrode and the value obtained by direct measurement were compared and never differed by more than a microvolt. The reproducibility of the constant electrode is shown by the following measurements. Two amalgams containing respectively 5 parts and 2.5 parts of

[1] Loc. cit.

zinc to 100 parts of mercury were put into two compartments of a cell. At 30° or below, these two amalgams should have the same potential, as solid zinc is present in both amalgams at or below this temperature.

Mar. 19th, 25° e. m. f. between the two was 0.000008 volt.
Mar. 25th, 20° e. m. f. between the two was 0.000006 volt.
Mar. 30th, 15° e. m. f. between the two was 0.000003 volt.
Apr. 19th, 25° e. m. f. between the two was 0.000002 volt.
May 6th, 30° e. m. f. between the two was 0.000000 volt.

Another of the advantages in measuring all potentials against the standard electrode is that the results from any two cells are directly comparable since the e. m. f. of any amalgam concentration cell is independent of the concentration of the electrolyte. It is only necessary to *accurately* control the temperature.

It was found convenient to express the concentrations as fractions the numerator giving the grams of zinc and the denominator the grams of mercury. The concentration of the standard electrode is then $\frac{2.220}{100}$ at 25°.

Cells charged with amalgams, gave as follows:

No. 1.

Days	*a* 2 phase	*b* $\frac{2.5}{100}$	*c* $\frac{2}{100}$	*d* $\frac{1}{100}$	*e* $\frac{1}{1000}$
At 25°					
1	—	—	0.000878	0.007780	0.035470
2	—	—	0.000875	0.007782	0.035470
Put at 30°	—	—	—	—	—
5	—	0.000005	0.000887	0.007787	0.035520
At 30°					
1	—	—	0.001670	0.008712	0.036920
2	—	—	0.001722	0.008771	0.036961
3	—	—	0.001728	0.008777	0.036964
At 20°					
1	—	0.000010	0.000047	0.006800	0.034064
2	—	0.000005	0.000040	0.006796	0.034057
3	—	0.000010	0.000047	0.006800	0.034075
At 15°					
1	—	0.000003	0.000015	0.005797	0.032585
4	—	0.000000	0.000003	0.005782	0.032579
6	—	—	0.000002	0.005784	0.032589

No. 2.

Days	2 phase	2.5/100	2/100	1/100	1/1000
At 0°					
1	—	0.000001	0.000009	0.002745	0.028110
2	—	—	—	0.002730	0.028195
4	—	—	—	0.002660	0.028054
10	—	—	—	0.002551	0.027892
11	—	—	—	0.002536	0.027881
At 30.02°					
1	—	0.000005	0.001740	0.008796	0.037160
5	—	0.000000	0.001731	0.008794	0.037180
6	—	—	0.001734	0.008794	0.037190
At 35°					
1	—	0.000668	0.002680	0.009883	0.038768
2	—	0.000845	0.002861	0.010070	0.038980
4	—	0.000774	0.002800	0.010017	0.038945
10	—	0.000618	0.002630	0.009846	0.038815
12	—	0.000615	0.002635	0.009861	0.038800
At 25°					
2	—	0.000002	0.000892	0.007800	0.035614
6	—	0.000001	0.000887	0.007792	0.035609

No. 3.

Days	2 phase	2.2/100	2/100	1.8/100	1 4/100	0.5/100
At 25°						
1	—	0.000068	0.000675	0.001640	0.004060	0.015432
3	—	0.000074	0.000875	0.001829	0.004253	0.015620
4	—	0.000047	0.000873	0.001829	0.004260	0.015625
At 30°						
1	—	0.001368	0.002222	0.003200	0.005680	0.017255
4	—	0.000850	0.001712	0.002680	0.005172	0.016759
5	—	0.000862	0.001720	0.002694	0.005183	0.016760
Back at 25°						
5	—	0.000060	0.000880	0.001831	0.004262	0.015650

Solubility of Zinc in Mercury.—The e. m. fs. between the two-phase electrode and amalgams varying in concentration from 1/100 to 2.5/100 have been plotted against the temperature in Fig. 6. The points for any one amalgam lie in a straight line, showing that the temperature coefficient is constant for this range of temperature. The points at which these lines cut the line of zero potential should represent the tempera-

tures at which these amalgams become saturated. By interpolation the solubility of zinc in mercury at any temperature within the range may be calculated. For example, it is seen that a line which would cut the line of zero potential at 25° would represent an amalgam of somewhat greater concentration than 2.2/100. At this point the decrease in e. m. f. with an increase in concentration is fairly uniform, an increase of 0.1/100 in concentration representing a decrease of about 0.000395, in e. m. f. The e. m. f. of the 2/100 amalgam at 25° is 0.000875; dividing this by 0.000395 we find that an increase of

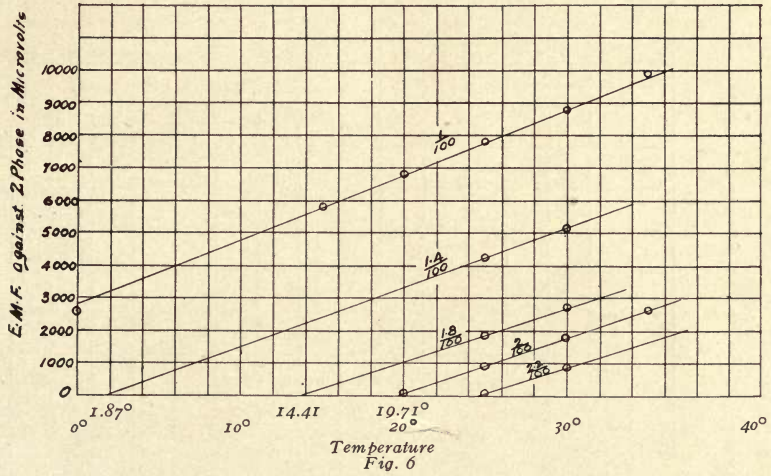

Fig. 6

0.221/100 in concentration would cause the amalgam to give zero potential, that is, the saturated amalgam at 25° contains 2.221 grams of zinc to 100 grams of mercury. This value is in good agreement with the average value, 2.220 (page 13), obtained from the density determinations and from the analyses. We have then three independent methods of determining the composition of a zinc amalgam.

The temperatures at which the lines on Fig. 6 cut the line of zero potential are given below:

Amalgam	Temperature at which line cuts line of zero potential
1.4	1.87°
1.8	14.41
2.0	19.71

That is, at 1.87°, 100 grams of Hg should dissolve 1.4 grams of zinc, etc.

Saturated amalgams were made up, by the method already described, (page 10) at 0°, 15° and 30°, and analyzed.

0°		15°		30°	
A	B	A	B	A	B
1.387	1.388	1.832	1.827	2.431	2.432
Average 1.3875		1.830		2.4315	

From these three results and the one already obtained for 25°, the solubility curve is plotted and shown in Fig. 7.

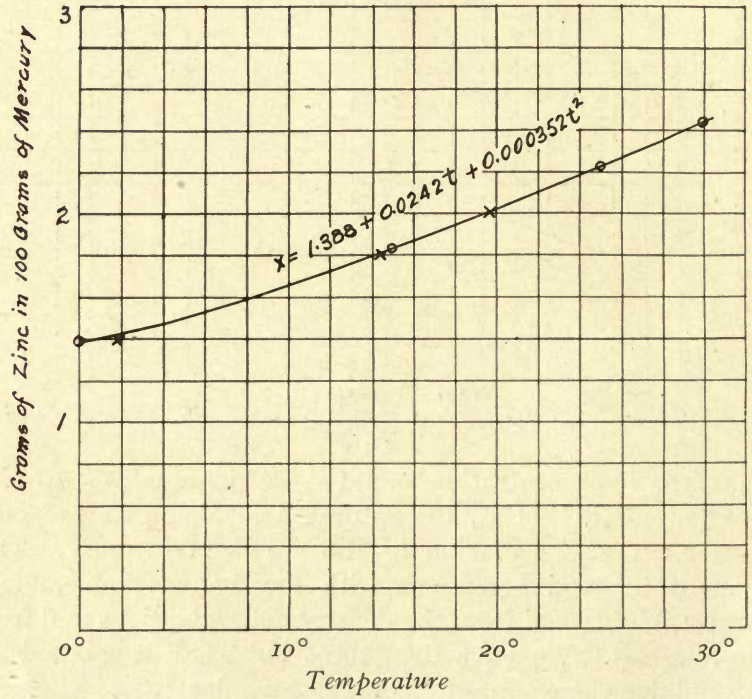

Fig. 7.

The points marked X are obtained from the intersections on Fig. 6 as already explained. The solubility of zinc in mercury may be very accurately expressed by the relation

$$X = 1.388 + 0.0242\,t + 0.000352\,t^2,$$

where X represents the number of grams of zinc in 100 grams

of mercury, and t the temperature. E. Cohen and Inouye[1] have recently determined the solubility of zinc in mercury from 0° to 100° and their results up to 50° are represented by the above equation. For temperatures above 50° a term containing t^3 would have to be added.

The Temperature Coefficient of Zinc Amalgam Cells.—As shown in the tables, the e. m. f. of the concentrated amalgams was measured at 0°, 15°, 20°, 25°, 30° and 35°. At 25° the temperature of the thermostat did not vary more than a few thousandths; at the other temperatures, not more than 0.01°. In order to keep the temperature constant at the higher temperatures it was found necessary to cover the thermostat with a box made of asbestos board. A small incandescent bulb kept the temperature of the air within this box a few degrees below that of the thermostat. Two thermometers calibrated by the Reichsanstalt were used in determining the temperatures. These thermometers were checked at the transition point of Glauber salt 32.383°.

The value of $\frac{d\pi}{d\mathrm{T}}$ of each amalgam measured against the constant electrode is given below:

Concentration	$\frac{d\pi}{d\mathrm{T}}$	Diffs.
2/100	0.0001680	
		0.0000046
1.8/100	0.0001726	
		0.0000116
1.4/100	0.0001842	
		0.0000133
1.0/100	0.0001975	
		0.0000295
0.5/100	0.0002270	

The temperature coefficient for any pair of amalgams may be obtained by taking the difference between their temperature coefficients as measured against the constant electrode. For example, between amalgams 2/100 and 1/100 $\frac{d\pi}{d\mathrm{T}}$ = 0.0000295; between 1.8/100 and 1/100 $\frac{d\pi}{d\mathrm{T}}$ = 00.0000249, etc. As is well known, the e. m. f. between concentrated zinc amalgams does not agree with the Nernst formula:

[1] Zeit. f. phys. Chem., 71, 625.

$$\pi = \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

Cady[1] claimed that this discrepancy was due to the heat of dilution of the amalgams and proposed the formula

$$\pi = \frac{U}{nF} + \frac{RT}{nF} \ln \frac{c_1}{c_2}.$$

On comparing this equation with the well-known Gibbs-Helmholtz equation,

$$\pi = \frac{U}{nF} + T \frac{d\pi}{dT}$$

we see that if the equation of Cady holds true,

$$\frac{d\pi}{dT} = \frac{R}{nF} \ln \frac{c_1}{c_2}$$

as was pointed out by Cady himself.

In the following table the values of $\frac{d\pi}{dF}$ obtained experimentally are compared with those calculated from the above relation.

Concentration.	$\frac{d\pi}{dT}$ obs.	$\frac{d\pi}{dT}$ calc.	Percent	Lewis
2/100–1.8/100	0.0000046	0.0000045	0.0000045	0.0000043
2/100–1.4/100	0.0000162	0.0000154	0.0000151	0.0000146
2/100– 1/100	0.0000295	0.0000298	0.0000294	0.0000286
2/100–0.5/100	0.0000590	0.0000597	0.0000591	0.0000579
1.8/100–1.4/100	0.0000116	0.0000108	0.0000106	0.0000103
1.8/100– 1/100	0.0000249	0.0000253	0.0000250	0.0000243
1.8/100–0.5/100	0.0000544	0.0000552	0.0000546	0.0000535
1.4/100– 1/100	0.0000133	0.0000146	0.0000143	0.0000140
1.4/100–0.5/100	0.0000428	0.0000443	0.0000440	0.0000433
1/100–0.5/100	0.0000295	0.0000298	0.0000296	0.0000292

Expression of Concentration.—In calculating the values for the last three columns, the following values were given to the constants: R = 8.316; N = 2; F = 96,540. There has been considerable discussion as to the best method of expressing concentrations in a case of this kind. In the last three columns three different methods of expressing concentrations are employed, and since the concentrations employed are

[1] Jour. Phys. Chem., 2, 551 (1898).

fairly great the different methods give considerably different results. In the first calculated column the concentrations are expressed as grams of zinc in grams of mercury. In the second, the concentrations are expressed as grams of zinc in grams of amalgam. In the last column, the concentrations are expressed according to the method suggested by Lewis,[1] which depends on the generalization that the activity of a substance is proportional to its mol fraction. That is, instead of calculating $\frac{d\pi}{dT}$ from the expression $\frac{R}{nF} \ln \frac{c_1}{c_2}$, the expression $\frac{R}{nF} \ln \frac{n}{n + N_1} \Big/ \frac{n}{n + N_2}$ is used, where n = the number of molecules of dissolved substance, and N_1 and N_2 the number of molecules of the solvent in the two amalgams respectively. On comparing the values in the three calculated columns with those in the observed column, it is seen that the values in the second calculated column are in much better agreement with the facts than either of the other two. Of course, as the dilution increases the three calculated values approach each other, and in the case of fairly dilute amalgams, it makes no difference as to which of the three methods of expressing the concentration is used. It was probably due to the fact that Richards[2] and his co-workers did not employ very concentrated amalgams that they failed to detect these really considerable differences due to the different methods of expressing the concentration. With the exception of the pairs of amalgams containing the one of 1.4/100 concentration (which for some reason seems to have given an incorrect value), all the values in column 2 agree with the observed values, within the experimental error. It appears, then, that the value of $\frac{d\pi}{dT}$ for zinc amalgams may be obtained from the relation $\frac{d\pi}{dT} = \frac{R}{nF} \ln \frac{c_1}{c_2}$, if the concentrations are expressed as *grams of zinc in grams of amalgam*, as accurately

[1] Jour. Amer. Chem. Soc., **30**, 668 (1908).

[2] Publication No. 118, Carnegie Institution of Washington.

as from any experimental methods now within our reach.

The Gibbs-Helmholtz Equation.—From the data already given, a great many heats of dilution of zinc amalgams may be calculated by means of the Gibbs-Helmholtz equation

$$Q = nF\left(\pi - T\frac{d\pi}{dT}\right).$$

Concentration	π	$\frac{d\pi}{dT}$	Q calc. at 25°
2/100 – 1/100	0.006905	0.0000294	— 85.56
2/100 –0.5/100	0.014730	0.0000590	—132.81
1.8/100 – 1/100	0.005966	0.0000249	— 67.03
1.8/100 –0.5/100	0.013791	0.0000544	—111.56
1/100 –0.5/100	0.007825	0.0000296	— 45.92
0.2/1000– 1/1000	0.008702	0.0000298	— 8.21

As was to be expected, the heat of dilution grows less as the dilution increases, and beyond the dilution of 1/1000 it should become equal to zero since the potentials of zinc amalgams obey the gas laws beyond that dilution. The actual measurement of the heat of dilution is exceedingly difficult, on account of the experimental difficulties involved. There is little doubt that all of the results obtained by previous workers have been seriously in error. Unless all oxidation of the zinc is prevented, the results cannot be relied upon, since the heat of oxidation of zinc is so great that a proportionally small amount of oxidation would neutralize any cooling effect caused by the dilution. A special study has been made of these conditions, and it is hoped that the results will be ready for publication in the near future.

The Reduction of Zinc by Mercury

If a mixture of two metals be brought into a solution of their salts, one metal will go into solution while an equivalent amount of the second will be precipitated until the equilibrium condition is reached. The condition of equilibrium is:

$$A - F_1 + \frac{RT}{n_1}\ln\frac{P_1}{p_1} + F_2 - \frac{RT}{n_2}\ln\frac{P_2}{p_1} = 0$$

the well-known equation derived by Nernst[1] in which P_1

[1] Zeit. phys. Chem., 22, 539 (1897).

represents the solution tension of the first metal, p_1 the osmotic pressure of its ions in solution, n_1 its valence, F_1 the difference in potential between the metal and the solution; the same letters with the subscript (2) refer to the second metal. A, represents the difference of potential between the two metals, R, the gas constant, and T, the absolute temperature. In the case of an amalgam $F_1 = F_2$ and $A = O$, so that the above equation reduces to:

$$\frac{RT}{n_1} \ln \frac{P_1}{p_1} = \frac{RT}{n_2} \ln \frac{P_2}{p_2} \text{ or, } \sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}.$$

Ogg[1] has verified the above equation in the system mercury, silver nitrate and water. In this case the equilibrium concentrations are of sufficient magnitude to be determined analytically. Hulett and De Lury[2] found evidence of a definite equilibrium in the system mercury, cadmium sulphate and water.

If mercury is shaken with a zinc sulphate solution we may expect some mercury to go in solution and some zinc to be precipitated into the mercury forming a very dilute amalgam. As in the case of cadmium the concentrations involved in this equilibrium are too small to be determined by chemical means, but since the e. m. f. between the two zinc amalgams is proportional to their relative concentrations it was thought that a determination of the potentials of very dilute amalgams would indicate at least the order of magnitude of these equilibrium concentrations.

Cell No. 2 with the following amalgams at 25° gave:

Days	2 phase $\frac{2.220}{100}$	b $\frac{2}{10^3}$	c $\frac{1}{10^3}$
1	—	0.026768	0.035465
2	—	0.026764	0.035470
15	—	0.026773	0.035479

The $\frac{1}{10^3}$ amalgam remained practically constant at

[1] Ibid., **27**, 285 (1898).

[2] Jour. Am. Chem. Soc., **30**, 1805 (1908).

0.035470 for a week, which was the same value as was observed for an amalgam of the same concentration in cell No. 1.

Cell No. 6 had six compartments. One compartment contained the standard electrode, the next four contained weighed amounts of mercury, and into the sixth were put 60.7021 grams of mercury and 0.00607 gram of zinc making a $\frac{1}{10^4}$ amalgam. The cell was then sealed off and put at 25°. The e. m. f. of this $\frac{1}{10^4}$ amalgam against the constant electrode was:

5 hours	0.064937
7 hours	0.064995
10 hours	0.065000
1 day	0.065226

There is some evidence of a drift here, but the e. m. f. was practically constant at 0.065000 for some time.

The cell was now taken out of the thermostat and was rocked and the wire glowed for several days to remove any residual oxygen before depositing the mercury in the other compartments to form the more dilute amalgams. The cell was then warmed up to about 35° before it was put back in the 25° bath as it had been found that the two-phase electrode came to equilibrium more quickly from the higher temperature.

In depositing zinc in the mercury a storage battery of 120 volts was closed over large external resistances which included an accurately calibrated set; after the circuit was closed the fall of potential over 1000 ohms was measured with the potentiometer. The internal resistance was so small that the current was practically the same before and after the cell had been switched into the circuit, so that the time necessary for each deposition was calculated before the cell was switched into the circuit. The time was taken with a stop watch and the fall in potential over 1000 ohms was measured at frequent intervals during the time the current was depositing zinc.

Compartment (*b*) contained 35.0004 grams of mercury and it was desired to deposit 0.00035 gram of zinc from the two-phase electrode.

At	9.15	circuit was closed.			
"	9.16	fall of potential over	1000	ohms was	0.19947 v.
From	9.20 to 9.50	" "	"	"	0.19941 v.
At	9.55	" "	"	"	0.19945 v.
"	10.05	" "	"	"	0.19950 v.
"	10.10	" "	"	"	0.19958 v.
"	10.15	" "	"	"	0.19970 v.
"	10.18	" "	"	"	0.19993 v.
"	10.20	" "	"	"	0.20010 v.
"	10.25	" "	"	"	0.20018 v.
"	10.30	" "	"	"	0.20004 v.
"	10.35	" "	"	"	0.20008 v.
"	10.38	" "	"	"	0.20015 v.
"	10.41	broke the circuit.			

The average value of the current was 0.00019964 which flowed for one hour, twenty-six minutes or 5160 seconds and gave 1.0301 coulomb. As one coulomb deposits 0.0003385 gram of zinc there was deposited in the 35 grams of mercury 0.0003486 gram of zinc.

Immediately after the circuit was broken the cell was rocked and the measurements of this amalgam against the constant electrode were taken.

1 minute	0.094707
5 minutes	0.094705
11 minutes	0.094704
10 hours	0.094883
15 hours	0.094944

There was no drift here for several hours. The value 0.09470 is evidently the correct one for this $1/10^5$ amalgam (the current was broken somewhat too soon so that the concentration of this amalgam was really $0.996/10^5$).

Zinc was now deposited in the 34.9902 grams of mercury in compartment *c*. The current was 0.00011814 which remained absolutely constant for the fourteen minutes and thirty-five seconds it was depositing zinc. This gave 0.10336 coulomb which deposited 0.00003487 gram of zinc. It was found necessary to rock the cell for about five minutes before the readings became at all constant.

5 minutes	0.12448
10 minutes	0.12453
15 minutes	0.12462
20 minutes	0.12471
25 minutes	0.12471
35 minutes	0.12480

There is evidence of considerable loss here. The original value of about 0.1245 is probably near the correct one.

Compartment *d* contained 34.9889 grams of mercury. A current of 0.0001175 was passed for 88 seconds which gave 0.010341 coulomb and deposited 0.000003500 gram zinc. The cell was rocked for two minuts and then measured.

2 minutes	0.151+
3 minutes	0.153+
4 minutes	0.1550
5 minutes	0.1555
6 minutes	0.1558
7 minutes	0.1562
10 minutes	0.1575
25 minutes	0.1587
12 hours	0.1664

The potential of this $1/10^7$ amalgam was variable during the first few minutes but at the end of four minutes it became constant enough to be followed in the fourth place decimal.

The value 0.1550 may be taken as an approximation to the correct value.

Compartment *e* contained 34.9849 grams of mercury. A current of 0.00001386 amp. for $75^1/_5$ seconds gave 0.0010423 coulomb and deposited 0.0000003525 gram of zinc. The cell was then rocked for one-half minute and measured.

1 minute	0.23+	7 minutes	0.435
2 minutes	0.35+	25 minutes	0.479
3 minutes	0.40+	30 minutes	0.511
4 minutes	0.41	4 hours	0.7031

The behavior of this $1/10^8$ amalgam was decidedly different from any previous one. The amalgam never became constant and in four hours the value had risen to 0.703 which is about the value that pure mercury falls to when allowed to stand in an oxygen free zinc sulphate solution.

A great many measurements have been made on pure mercury against the two-phase standard in these cells, the same precautions being used to exclude oxygen as in the case of the dilute amalgams. The value at first was about 1.09 but in time settled down to about 0.74, usually something less than 0.75. After four hours, then, there was no more zinc in the $1/10^8$ amalgam than there was before any zinc had been deposited by the current.

After three days zinc was again deposited in this mercury in compartment *e*. It was thought probable that the amalgam had lost some zinc while the current was still depositing it, so a larger current was used. 0.000123 ampere for $8^4/_5$ seconds gave 0.001084 coulomb and deposited 0.0000003669 gram of zinc.

After	1 minute	the e. m. f. was 0.18+
After	2 minutes	the e. m. f. was 0.19
After	3 minutes	the e. m. f. was 0.21
After	5 minutes	the e. m. f. was 0.25
After	35 minutes	the e. m. f. was 0.50
After	2 days	the e. m. f. was 0.714

In this case where the time required to deposit the zinc was only about 1/10 of that previously used, a much lower value was obtained for the initial reading. This is also in good agreement with the idea of an equilibrium between the mercury and zinc sulphate, since the zinc from the first $1/10^8$ amalgam would have reduced the concentration of mercury ions in solution and so there would have been fewer present to remove the zinc from the second $1/10^8$ amalgam.

After three days this amalgam had apparently lost all of its zinc. Zinc was again deposited in this mercury by 0.00000235 amp. for $43^4/_5$ seconds, which gave 0.00010315 coulomb and deposited 0.00000003502 gram of zinc. The cell was rocked during the whole time of deposition:

1 minute	0.24
2 minutes	0.27
5 minutes	0.408
30 minutes	0.514

In a few hours the value rose to the equilibrium value of about 0.7+.

In the following table the e. m. f. measurements are given between amalgams varying in concentration from that saturated at 25° to one containing one part of zinc in one billion parts of mercury. In the column marked observed the value of each amalgam measured against the two-phase is given.

Amalgams	Observed V	Differences	Calculated
2.220/100	0.000000		
2/100	0.000890	0.000890	0.001340
1.8/100	0.001829	0.000939	0.001351
1.4/100	0.004260	0.002431	0.003226
1/100	0.007795	0.003535	0.004320
5/1000	0.015620	0.007825	0.008898
2/1000	0.026768	0.011148	0.029560
$1/10^3$	0.035470	0.008702	0.029560
$1/10^4$	0.065000	0.029530	0.029560
$1/10^5$	0.094700	0.029700	0.029560
$1/10^6$	0.12450	0.029800	0.029560
$1/10^7$	0.1550	0.030500	0.029560
$1/10^8$	0.185	0.0300	0.029560
$1/10^9$	0.24	0.0550	0.029560

The Nernst equation for concentration cells is $E = RT \ln C_1/C_2$ where C_1 and C_2 in our case represent the concentration of the zinc in the mercury. Changing to Briggs' logarithms for 25° we get $V = 0.029560 \log C_1/C_2$.

As has been observed by previous workers the e. m. f. between the concentrated amalgams is much too small to agree with the above equation. There is very good agreement in the range from 2/1000 to $1/10^7$ and even to $1/10^8$ if the first reading is taken.

In the case of amalgams more dilute than $1/10^8$ it was impossible to take any measurements before the amalgam had lost part of its zinc. In fact, the potential measurements seem to leave no doubt that in a short time both the $1/10^8$ and the $1/10^9$ amalgams had lost all of the zinc that had been deposited in them. It is well known that oxygen dissolved in the solution about a zinc amalgam does remove the zinc. There is little doubt that the glowing platinum wire in the cell

removed all oxygen from the vapor phase and it seems that the agitation of the electrolyte for days with the two-phase amalgam, which contained over 200 million times as much zinc as the $1/10^8$ amalgam, would have removed any residual oxygen from the solution. Considering all of these points it seems very unlikely that zinc was removed from these very dilute amalgams by oxygen.

The equilibrium between mercury and zinc in the amalgam and in solution undoubtedly follows the relation:

$$\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$$

where P_1 and P_2 represent the concentrations of zinc and mercury in the amalgam and p_1 and p_2 their respective concentrations in solution. In our case, P_2, the concentration of mercury in the amalgam, and p_1, the concentration of zinc in solution, are constant. The mercury in solution is mercurous mercury, but as has been shown by Ogg[1] the ions are composed of two atoms each and carry a double charge so that $n_2 = 2$ and for zinc $n_1 = 2$. The equation reduces to $P_1 \times p_2 = K$ and K is evidently a very small number. If mercury is brought into a zinc sulphate solution mercury should go into solution and zinc be deposited in an equivalent quantity in the mercury until the equilibrium constant has been satisfied. The measurements of the e. m. f. between pure mercury and the two-phase electrode have indicated this very thing. The initial high value of about 1.09 has always settled down to about 0.7+ indicating a deposition of zinc in the mercury. This reaction must be electrolytic so that when one double gram atom of mercury has passed into solution a gram atom of zinc has been deposited. It is thus seen that the actual concentration of zinc in the mercury is dependent upon the relative volumes of mercury and solution, at the same time the reaction must proceed until $P_1 \times p_2 = K$. Before any zinc was deposited in the mercury in cell No. 6

[1] Loc. cit.

the e. m. f.'s between the two-phase amalgam and the mercury in the different compartments were measured. It may be observed that this same gradation of values has been found in many other cases so that this may not be considered a chance effect.

A	B	C	D	E	F
Two phase	Mercury	Mercury	Mercury	Mercury	$1/10^4$
—	0.97	1.00	1.04	1.01	X

From these values it appears that the mercury nearest the compartments containing amalgams had acquired the most zinc. In the case of the two-phase amalgam, P_1 of the above equation is constant and relatively very large so that p_2 must be relatively very small. This amalgam would then tend to remove the mercury ions thrown into solution by the pure mercury in the other compartments so that the mercury in the compartments near by would have to continue giving ions to the solution in order to preserve the equilibrium.

When zinc was deposited electrolytically in the mercury, mercury was also deposited in proportion to their concentrations, but since the solution was saturated with zinc sulphate, while the concentration of mercury was exceedingly small, it is safe to assume that the zinc deposited corresponded to the coulombs passed even in the most dilute amalgams. The deposition of zinc disturbed the equilibrium and the zinc began at once to leave the amalgam and replace the mercury ions in solution until the equilibrium condition was again reached. In the cell used where the volume of mercury was about $^1/_6$ of that of the electrolyte, the equilibrium e. m. f. between mercury and the constant electrode fell to about 0.7+ and could be reached from either side.

It seems that the concentrations of our $1/10^8$ and $1/10^9$ amalgams were of the order of magnitude of the concentration of the mercury ions in solution. As was to be expected, this is a somewhat greater dilution than was found by Hulett and De Lury[1] in the case of cadimum amalgams.

[1] Loc. cit.

Summary

The chief results of this investigation are:

The determination of the solubility of zinc in mercury between 0° and 30°, represented by the equation

$$X = 1.388 + 0.0242\,t + 0.000352\,t^2$$

where X = grams of zinc in 100 grams of mercury, and t = the temperature.

The determination of the relation,

$D = 13.5340 - 0.0859\,p - (0.00244 - 0.000067\,p)\,(t - 25)$ (where p = grams of zinc in 100 grams of mercury, D = density of the amalgam, and t = the temperature) between the density and composition of zinc amalgams.

Measurements on the electromotive forces of zinc amalgams at 25° extending from the saturated amalgam to a dilution of 1 part of zinc to one billion parts of mercury. The observations were all based on a constant reproducible electrode and so are directly comparable.

The accurate measurement of $\frac{d\pi}{d\mathrm{T}}$ for zinc amalgam cells which would seem to indicate that $\frac{d\pi}{d\mathrm{T}}$ can be very accurately calculated by the equation

$$\frac{d\pi}{d\mathrm{T}} = \frac{\mathrm{R}}{n\mathrm{F}} \ln \frac{c_1}{c_2}$$

if we express the concentrations as grams of zinc in grams of amalgam. It is shown that for this calculation this method of expressing concentrations is superior to any other proposed.

The discovery of a region between one gram of zinc to 1000 grams of mercury, and one gram of zinc to 10 million grams of mercury where the potential between any two amalgams conforms to the requirements or the gas laws. Beyond this dilution the potential fell off so rapidly with the time that no accurate measurements could be taken, which indicates that the reaction $Zn + \overset{++}{Hg}_2 \rightleftarrows \overset{++}{Zn} + 2Hg$ is a reversible one and that a definite equilibrium is established in the system mercury, zinc sulphate and water.

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